Field volatility of Dicamba

Report:	MRID 50578902. Duncan, B., Beachum, C.E., and Sall, E.D. 2017. Field Volatility of Spray Solutions Containing Tank-mixed Diglycolamine Dicamba (MON 76980) and Potassium Glyphosate (MON 79789) for Pre- and Post-Emergent Treatments in 2016 Texas Field Trial. Unpublished study performed by Monsanto Company, St. Louis, Missouri; AgGro Innovations, LLC, Cypress, Texas; Stone Environmental, Inc., Montpelier, Vermont; and AGVISE Laboratories, Northwood, North Dakota; sponsored and submitted by Monsanto Company, St. Louis, Missouri. Monsanto Study No.: STC-2016-0545. Reference ID: MSL0028469. Study completion May 15, 2017. Report completion November 16, 2017.
Document No.:	MRID 50578902
Guideline:	OCSPP 835.8100
Statements:	The study was conducted in compliance with FIFRA GLP standards except for test site information, study weather data from external sources, pesticide and crop histories, soil taxonomy information, and test plot preparation prior to application (p. 3). Signed and dated Data Confidentiality, GLP Compliance, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-6).
Classification:	This study is **acceptable**. Dicamba was detected in pre-application samples from both plots. An independent laboratory method validation was not conducted.
PC Code:	128931

Final EPA Reviewer:	William Eckel Senior Advisor	Signature: William P. Eckel Date: Digitally signed by William P. Eckel Date: 2018.10.31 11:01:24 -04'00'
Final EPA Reviewer:	Chuck Peck Senior Fate Scientist	Signature: Chuck Peck Date: 2018.10.31 10:45:10 -04'00'
CDM/CSS-Dynamac JV Reviewers:	Richard Lester Environmental Scientist	Signature: Richard R Lester Date: 8/14/18
	Joan Gaidos, Ph.D. Environmental Scientist	Signature: Joan Gaidos Date: 8/14/18

This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel. The CDM/CSS-Dynamac Joint Venture role does not include establishing Agency policies.

Executive Summary

Field volatilization of dicamba formulation MON 76980 when tank mixed with potassium glyphosate (MON 79789) was examined from a bare plot and a cropped cotton plot in Fort Bend

County, Texas. The site where the study was conducted was about 4 miles west of Beasley, Texas and about 3 miles north of Kendleton, Texas. The experiments were conducted for about 72 hours following application. The application method was spray application at a nominal application rate of 0.5 lbs. a.e./A. The treated plots were about 700 m apart. No control plot was established.

Under field conditions at the bare ground plot, based on calculations using the Integrated Horizontal Flux method, a peak volatile flux rate of 0.001665 $\mu g/m^2 \cdot s$ was measured accounting for 0.032% of the applied dicamba observed 0 to 3 hours post-application. By the end of the study, a total of 0.104% of dicamba volatilized and was lost from the field. No true secondary peak volatile flux rates were observed. Flux rates are depicted in **Figure 1**.

Under field conditions at the cotton plot, based on calculations using the Integrated Horizontal Flux method, a peak volatile flux rate of 0.001954 $\mu g/m^2 \cdot s$ was measured accounting for 0.045% of the applied dicamba observed 0 to 3 hours post-application. By the end of the study, a total of 0.109% of dicamba volatilized and was lost from the field. No true secondary peak volatile flux rates were observed. Flux rates are depicted in **Figure 2**.

Figure 1 Volatile flux using the Integrated Horizontal Flux Method – Bare Plot

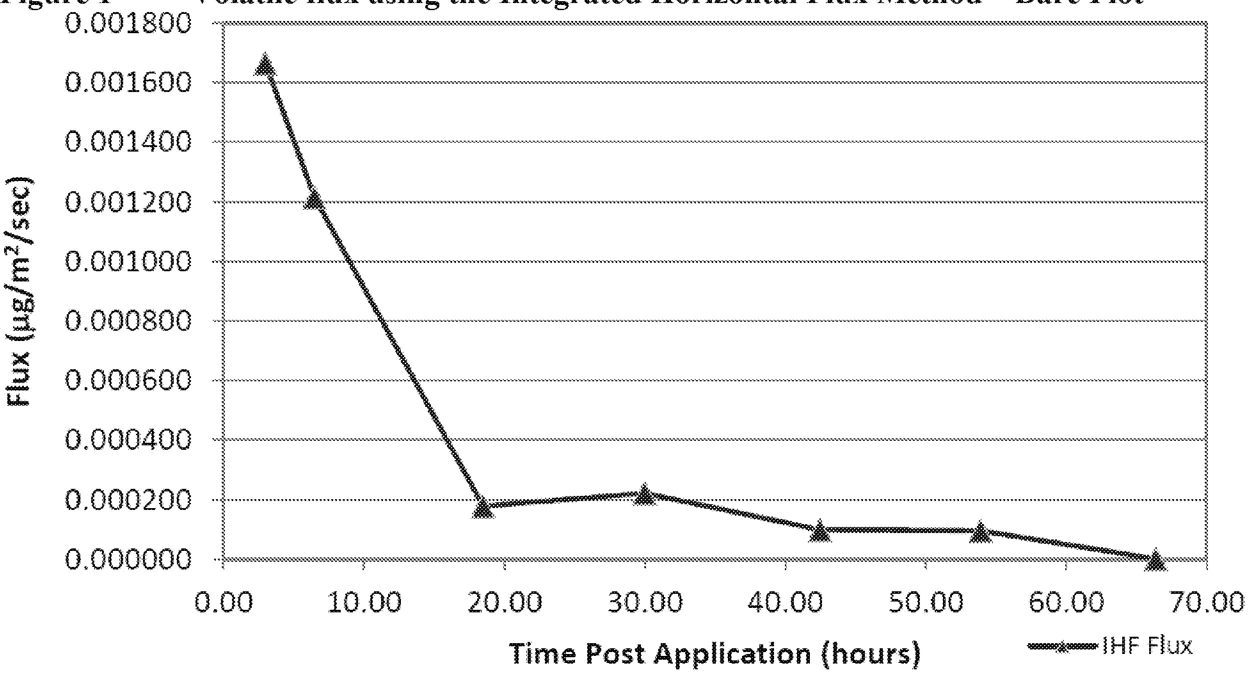
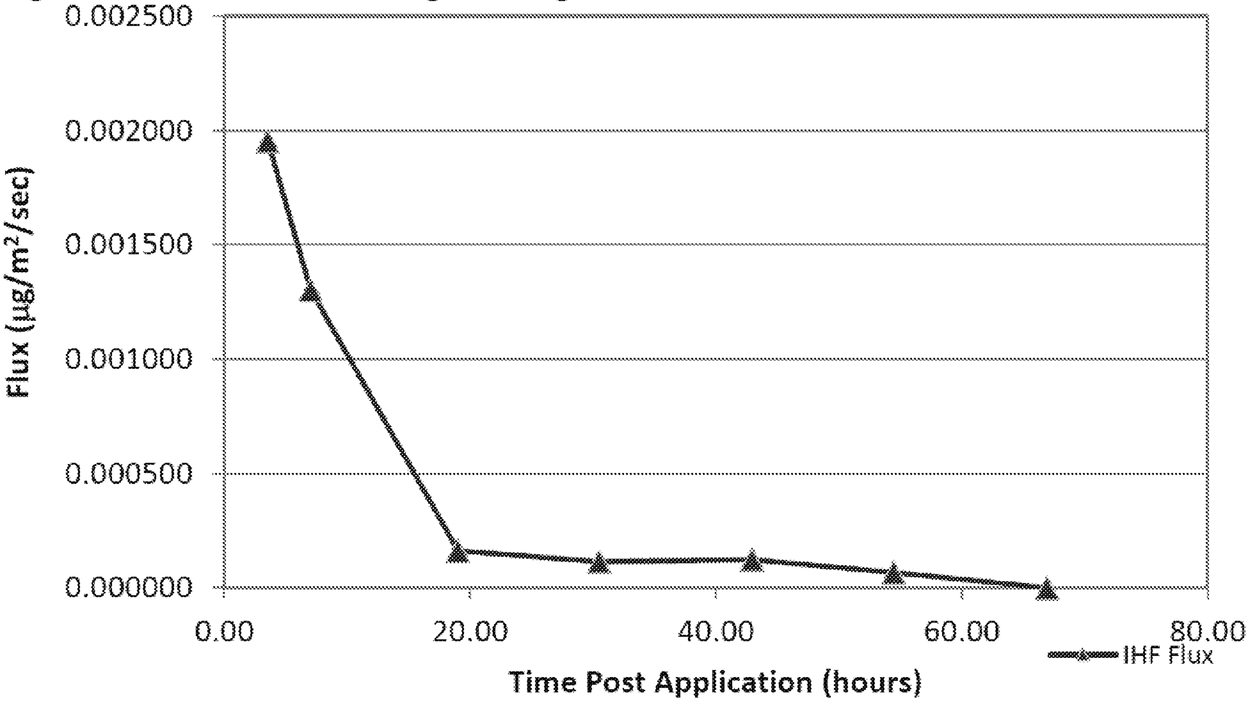
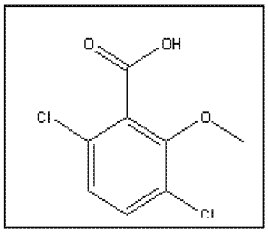


Figure 2 Volatile flux using the Integrated Horizontal Flux Method – Cotton Plot



I. Materials and Methods

A. Materials



1. Test Material

Product Name: MON 76980 (dicamba, p. 13)
Formulation Type: Liquid (p. 14)
CAS #: 104040-79-1 (p. 14)
Storage stability: The expiration date of the test substance was July 7, 2017 (p. 14). Working solutions used during analysis of application verification filter papers had a two-month shelf life at <10°C (Appendix 6, p. 128). Solutions containing dicamba prepared in absolute ethanol or acetonitrile and stored at about 4°C have been demonstrated stable for at least 201 days.
Product Name: MON 79789 (potassium glyphosate, p. 14)
Formulation Type: Liquid (p. 14)
CAS #: 70901-12-1

2. Storage Conditions

The test substance was received on September 19, 2016 (p. 15). Storage and transport temperatures were monitored, and maximum and minimum temperatures were recorded (p. 15). The study protocol indicates the test substance would be stored under label conditions in a monitored pesticide storage area adequate to preserve stability (Appendix 10, pp. 296-297).

B. Study Design

1. Site Description

The test site was located in Fort Bend County, Texas about 4 miles west of Beasley, Texas and about 3 miles north of Kendleton, Texas (p. 16). One bare ground test plot and one cotton-cropped test plot were used in the study. The plots were separated by about 700 m (0.7 km; p. 17). The test sites were uniform with respect to soil texture and vegetation, and nearly uniform regarding slope, between 0% and 2% (p. 16). Areas surrounding the test plots were agricultural land (Figure 1, p. 63).

The bare ground plot was about 450 feet in length and 450 feet in width with a total treated area of about 4.6 acres (p. 17). The USDA textural class for the soil was clay loam (Table 1, p. 41). Crop history in the three years preceding the study included grain sorghum and cotton (Appendix 1, pp. 80-81). Numerous fertilizers and pesticides were applied to the field in the three years preceding the study (Appendix 1, pp. 80-81).

The cotton test plot was about 630 feet in length and 630 feet in width with a total treated area of about 9.1 acres (p. 17). The USDA textural class for the soil was clay (Table 1, p. 41). Crop history in the three years preceding the study included corn and cotton (Appendix 1, pp. 82-84). Numerous fertilizers and pesticides were applied to the field in the three years preceding the study (Appendix 1, pp. 82-84).

2. Application Details

Application rate(s):	The target application rate was 0.5 lb a.e./A or 12.07 gal/A (pp. 20-21, 38). For each test plot, ten application monitoring sampling stations, each consisting of five filter paper samples were positioned in the spray area to verify the application rate (pp. 23-24). Spray application rates were also calculated using swath pass times, dimensions of the spray swaths, the target application rate, and the calibrated total boom output (p. 35). Calculated applications rates were 11.93 GPA or 0.493 lbs a.e./A for the bare ground plot and 12.00 GPA or 0.496 lbs a.e./A for the cotton plot (Table 3, p. 43). Average recovery values for the application monitoring samples were 95.7% and 93.5% of the theoretical application rate for the bare ground and cotton plots, respectively (p. 35).
Irrigation and Water Seal(s):	No irrigation or water seals were used during the study.
Tarp Applications:	Tarps were not used.
Application Equipment:	A Hagie DTS-10 ground sprayer equipment with a 90 ft boom was used for the spray application (pp. 20-21). 60 Turbo TeeJet®

Induction (TTI) 11003 nozzles were installed with 18-inch spacing and a boom height above the ground or crop set at 20 inches. The sprayer had two spray tanks with a volume of 400 gal. each.

Equipment Calibration Procedures: Nozzle uniformity was tested by spraying water at a pressure of 40 psi through the boom and measuring nozzle output using SpotOn® Model SC-1 sprayer calibrator devices (p. 21). Each nozzle was tested three times to determine variability. Calibration of the sprayer and nozzles established the total boom output per minute of spray to be 17.55 GPM. The forward speed of the sprayer tractor was calibrated by timing the duration required, in seconds, to drive a known distance of 250 feet. Speed verification was repeated three times.

Application Regime: The application rates and methods used in the study are summarized in **Table 1**.

Table 1. Summary of application methods and rates for MON 76980

Field	Application Method	Time of Application (Date and Start Time)	Amount Dicamba Applied[1] (lbs)	Area Treated (acres)	Calculated Application Rate (lb ae/acre)	Reported Application Rate (gal/acre)
Bare	Spray	10/4/2016 12:18	2.3	4.6	0.493	11.93
Cotton	Spray	10/4/2016 11:33	4.5	9.1	0.496	12.00

Data obtained from p. 22; and Table 3, p. 43 of the study report.
[1] Reviewer calculated as calculated application rate (lb a.e./acre) × area treated (acres).

Application Scheduling: Critical events of the study in relation to the application period are provided in **Table 2**.

Table 2. Summary of MON 76980 application and monitoring schedule

Field	Treated Acres	Application Period	Initial Air/Flux Monitoring Period	Water Sealing Period	Tarp Covering Period
Bare	4.6	10/4/16 between 12:18 – 12:28	10/4/16 between 12:11 – 12:31	Not Applicable	Not Applicable
Cotton	9.1	10/4/16 between 11:33 – 11:49	10/4/16 between 11:20 – 11:55	Not Applicable	Not Applicable

Data obtained from p. 22 and Table 8, p. 48 of the study report.

3. Soil Properties

Soil properties measured before the study are provided in **Table 3**.

Table 3. Summary of soil properties for fields/plots

Field	Sampling Depth (inches)	USDA Soil Textural Classification	USGS Soil Series	WRB Soil Taxonomic Classification	Bulk Density (g/cm^3)	Soil Composition
Bare	0-6	Clay Loam	Not Reported	Not Reported	1.19	% Organic Carbon[1] = 1.0% % Sand = 23% % Silt = 40% % Clay = 37%
Cotton	0-6	Clay	Not Reported	Not Reported	1.16	% Organic Carbon[1] = 1.2% % Sand = 21% % Silt = 34% % Clay = 45%

Data obtained from Table 1, p. 41 of the study report.
[1]Reviewer calculated as: organic carbon (%) = organic matter (%)/1.72. Organic matter was reported as 1.8% for the bare ground plot and 2.0% for the cotton plot.

A Custom Soil Resource Report for Fort Bend County, Texas classified soils in the bare ground plot as Lake Charles Clay, Bernard Clay Loam, and Edna Loam (Appendix 2, pp. 93-95). Soils in the cotton plot are classified Lake Charles Clay.

Soil moisture at 1/3 Bar for 0-6" composited soil samples was reported as 32.4% for the bare ground plot and 38.8% for the cotton plot (Table 1, p. 41). Soil moisture at 15 Bar was reported as 18.7% and 21.4% for the bare ground plot and cotton plot, respectively. The maximum volumetric soil moisture at a depth of 2 inches was 0.3054 for both plots (Table 4, p. 44).

Maximum soil temperatures for the bare ground plot were 111.4°F (44.1°C), 81.7°F (27.6°C), and 79.5°F (26.4) at the surface, 2 inches, and 6 inches, respectively (Table 4, p. 44). Maximum soil temperatures for the cotton plot were 108.5°F (42.5°C), 80.7°F (27.1°C), and 79.1°F (26.2°C) at the surface, 2 inches, and 6 inches, respectively.

Insufficient information was provided to plot soil temperature and soil moisture measured throughout the study.

4. Meteorological Sampling

A meteorological station was erected about 1,500 feet (460 m) northeast of the cotton plot (p. 20 and Figure 1, p. 63). The station consisted of an Onset Computer Corporation HOBO® Weather Station H21-001 data logger and an Onset H21-002 microstation data logger with sensors for precipitation, soil moisture (2 inches), air temperature, relative humidity, soil temperature (at the surface, 2 inches, and 6 inches depth), solar radiation, wind speed, wind direction, and evapotranspiration (p. 20). All parameters were measured at one-minute intervals for the duration of the study from October 3 to 8, 2016.

A flux monitoring meteorological station was established near each test plot about 15 m from the northwest edge of the plots (p. 20). These monitoring stations recorded air temperature, wind speed, and wind direction. Gill Instruments WindSonic Option 3 (1405-PK-040) 2-dimensional sonic anemometers were used to record wind speed and direction data at heights of 0.33, 0.55, 0.90, and 1.5 m above the soil or crop surface. Air temperature and relative humidity were monitored at the same heights using Onset S-THB-M002 12-bit smart sensors. The flux meteorological station sensors were wired to Onset HOBO® RX3000 remote monitoring station data loggers.

Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in **Table 4**. The location of the meteorological equipment for each field is shown in **Attachment 3**.

Table 4. Summary of meteorological parameters measured in the field

Field	Minimum Fetch (m)	Parameter	Monitoring heights (m)	Averaging Period
Site Meteorological Station	Not Reported	Precipitation	1.5	1 minute
		Soil moisture	2 inches	1 minute
		Air temperature	1.5	1 minute
		Relative humidity	1.5	1 minute
		Soil temperature	Surface, 2 inches, 6 inches	1 minute
		Solar radiation	1.5	1 minute
		Wind speed/wind direction	1.5	1 minute
		Evapotranspiration	1.5	1 minute
Bare	74.67	Air temperature	0.33, 0.55, 0.90, and 1.5	Not Reported
		Windspeed/wind direction	0.33, 0.55, 0.90, and 1.5	Not Reported
		Relative humidity	0.33, 0.55, 0.90, and 1.5	Not Reported
Cotton	115.20	Air temperature	0.33, 0.55, 0.90, and 1.5	Not Reported
		Windspeed/wind direction	0.33, 0.55, 0.90, and 1.5	Not Reported
		Relative humidity	0.33, 0.55, 0.90, and 1.5	Not Reported

Data obtained from p. 20; Table 9, p. 49, and Appendix 7, pp. 271-272 of the study report.

5. Air Sampling

Two pre-application samples were collected at 0.15 m above the soil surface at the center of each test plot (p. 22). Samples were collected from the late evening of October 3 to the morning of October 4 for about 11 hours.

During application, eight off-field air monitoring stations were placed about 1.5 m above the soil surface and about 15 m from the edges and corners of the treatment area for each test plot (p. 23). The air samplers were turned on just prior to application and turned off immediately following application.

Following application, in-field air samplers were used for flux monitoring up to 72 hours following application (p. 24). Samplers were placed on a mast in the approximate center of each plot with air sampling pumps at heights of *ca.* 0.15, 0.33, 0.55, 0.90, and 1.5 m above the soil or crop surface.

6. Sample Handling and Storage Stability

PUF sorbent tube samples were always handled with nitrile gloves (p. 25). PUF sorbent tubes were placed in pre-labeled conical tubes. Pre-application, during application, post-application, spray area, field exposed spikes, and transit samples were stored and shipped in coolers containing dry ice until final transfer to cold storage at -20°C prior to laboratory analysis. Tank mix samples were stored and shipped under ambient conditions.

All PUF samples were extracted and analyzed within 22 days after collection (Appendix 6, p. 130). Stability of dicamba was demonstrated for at least 78 days during frozen storage in a stability study. All PUF samples were analyzed within one day of extraction which is within the demonstrated stability.

7. Analytical Methodology

- Sampling Procedure and Trapping Material: Flux monitoring equipment consisted of active air samplers mounted on metal posts (p. 18). The active samplers included a glass sorbent tube containing polyurethane foam (PUF) attached with plastic tubing to an air sampling pump. Both SKC PUF tubes (SKC Catalog Number 226-92) and custom hand-blown glass tubes of identical dimensions were used. Three models of air pumps were used: SKC AirChek® 52, SKC AirChek® XR5000, and SKC Universal PCXR8. Pumps were calibrated to a flow rate of 2.995-3.050 L/min (p. 19).

- Extraction method: The contents of the PUF sorbent tubes were extracted using methanol containing stable-labeled internal standard (Appendix 6, pp. 165-179). The sample was fortified with internal standard, a grinding ball was added to the tube, and 29.8 mL of methanol was added. The sample tubes were capped and agitated on a high-speed shaker (Geno/Grinder®) for 1200 cycles per minute for 30 minutes. The cap was removed and 1.8 mL of supernate was passed through a filter plate. The sample was evaporated to dryness under nitrogen at 50°C. The sample was reconstituted in up to 10-fold less volume of 25% methanol in water. The sample was mixed and analyzed by LC-MS/MS with electrospray ionization in negative ion mode within the storage time determined during method validation.

- Method validation (Including LOD and LOQ): Method validation was achieved by fortifying 9 replicate fortification samples at each of three fortification levels (0.3 ng/PUF, 3 ng/PUF, and 60 ng/PUF; Appendix 6, pp. 183-184). Validation assessments showed acceptable accuracy between 70% and 120% and precision (<20% RSD) for all fortified matrices at each fortification level. Average recoveries were 87%, 94%, and 94% at 0.3, 3, and 60 ng/PUF, respectively. No independent laboratory validation is provided. The method (ME-1902-01) was originally validated using 0.3 ng/PUF as the Limit of Quantitation (LOQ; Appendix 6, p. 130). However, for recent studies that used the method, the 0.3 ng/PUF QC samples were not successfully recovered. The LOQ was therefore raised to 1.0 ng/PUF for the method. No information is provided on a separate Limit of Detection (LOD).

- Instrument performance: Calibration standards were prepared at concentrations ranging from 0.15 to 75 ng/PUF (Appendix 6, p. 128). Concentrations were 0.15, 0.225, 0.3, 0.75, 1.5, 2.25, 3, 7.5, 15, 22.5, 30, and 75 ng/PUF (Appendix 6, pp. 172 and 247). Analyst® software was used to derive the calibration curve using a weighted linear curve (1/x; Appendix 6, pp. 178 and 195).

8. Quality Control for Air Sampling

Lab Recovery:	Most laboratory spike recoveries are within the acceptable range of 90-110%. Laboratory spike samples were prepared at fortification levels of 1 ng/PUF (21 samples), 3 ng/PUF (20 samples), 60 ng/PUF (21 samples), and 600 ng/PUF (6 samples; Appendix 6, Table 5, p. 139). Average recoveries were 90.3%, 92.4%, 93.9%, and 92.2% at 1 ng/PUF, 3 ng/PUF, 60 ng/PUF, and 600 ng/PUF, respectively. Recoveries ranged from 71.9% to 105%.
Field blanks:	A pre-application background level of 0.0436 ng/m^3 was measured at the bare ground plot and 0.0787 ng/m^3 at the cotton plot (Tables 10-11, pp. 50-51).
Field Recovery:	Most field spike recoveries were within the acceptable range. Six field spikes were fortified at each of 0, 3, and 600 ng/PUF. Dicamba was below the LOQ for the six blank control samples. Recoveries ranged from 89% to 109% for the 3 ng/PUF samples and 87% to 100% for the 600 ng/PUF samples (p. 34 and Appendix 6, Table 10, p. 144).
Travel Recovery:	Three transit controls (0 ng dicamba/PUF) were prepared along with three transit stability PUF samples fortified at 30 ng dicamba/PUF (p. 25). Recoveries from transit stability samples ranged from 27.7 ng/PUF (92%) to 28.6 ng/PUF (95%; p. 34 and Appendix 6, p. 145). Dicamba was detected in one of the three control samples at 0.629 ng/PUF, which is below the LOQ of 1 ng/PUF (Appendix 6, p. 206).
Breakthrough:	Samples that were fortified at 600 ng/PUF had an average recovery of 92.2% (Appendix 6, Table 5, p. 139). The highest dicamba amount measured on a PUF sample was 38.7 ng/PUF (Appendix 6, Tables 6-9, pp. 140-143) which is about 6% of the highest fortification, indicating that dicamba loss due to breakthrough is unlikely.

9. Application Verification

To verify the application, ten application monitoring stations were positioned in the spray area in each plot (pp. 23-24). Each monitoring station consisted of five filter paper samples on a wooden 2” × 6” × about 2.5’ board. The board was placed on the bare ground or at crop height for the cotton plot. Cardboard was affixed to the wooden board and five 150 mm diameter Whatman® filter papers were pinned to the cardboard. Sampling stations were positioned to capture various portions of the spray boom along a transect perpendicular to the direction of spray application at distances of 10, 15, 20, 25, or 30 ft from spray swath centers.

Spray application rates were calculated using swatch pass times, the dimensions of the spray swaths, the target amount of dicamba to be applied, and the calibrated total boom output (p. 35). Calculated application rates were within 0.2 GPA of the target application rate of 12.07 GPA. The percent of target dicamba applied was 98.9% for the bare ground plot and 99.4% for the cotton plot (Table 3, p. 43).

Measured application on the filter paper spray area samples was compared to the calculated spray application rates (p. 35). Average recoveries were 95.7% for the bare ground plot and 93.5% for the cotton plot (Table 7, p. 47). Recoveries achieved on filter paper spike samples ranged from 103% to 108% (Appendix 6, Table 3, p. 137).

Tank mix samples were also collected and analyzed to verify the amount of dicamba present in the tank mix (p. 23).

10. Deposition and Air Concentration Modeling

MRID 50578903, entitled "Deposition and Air Concentration Modeling for Dicamba Formulation MON 76980 Mixed with MON 79789" (Reiss and Popovic, 2017) was based on the results of MRID 50578902. Dry deposition, wet deposition, and air concentration estimates were calculated based on the flux rates measured in this study and relevant meteorological data. U.S. EPA's AERMOD model (version 15181) was used to estimate deposition, while the Probabilistic Exposure and Risk model for Fumigants (PERFUM, version 2.5) was used to estimate air concentrations (MRID 50578903, p. 8).

Three sets of estimates were calculated, using meteorological data for Raleigh, North Carolina; Peoria, Illinois; and Lubbock, Texas (MRID 50578903, p. 8).

Wet and dry deposition estimates were made at 10 distances from the field (5, 10, 20, 30, 40, 50, 75, 100, 125, and 150 m; MRID 50578903, p. 17). At a distance of 5 m from the edge of the field, maximum 24- hour average dry deposition ranged from 4.45×10^{-6} to 7.42×10^{-6} g/m^2 for applications to bare soil and 3.36×10^{-6} to 5.99×10^{-6} g/m^2 for applications to cotton. Maximum wet deposition ranged from 3.59×10^{-7} to 8.45×10^{-7} g/m^2 for applications to bare soil and 3.48×10^{-7} to 7.28×10^{-7} g/m^2 for applications to cotton. 90th percentile values were also calculated and were about 53 to 55% of the maximum values for dry deposition and 1 to 5% of the maximum values for wet deposition.

Modeled dicamba air concentrations were calculated at 4 distances from the field (5, 10, 25, and 50 m). The 95th percentile of the modeled air concentrations ranged from 38.2 to 63.1 ng/m^3 and 10.0 to 15.6 ng/m^3 for 1 and 24-hour averaging periods, respectively, for applications to bare soil and 30.7 to 49.3 ng/m^3 and 8.1 to 12.6 ng/m^3 for 1 and 24-hour averaging periods, respectively, for applications to cotton (MRID 50578903, p. 24).

The reviewer has confirmed deposition and air concentration estimates generated in MRID 50578903.

II. Results and Discussion

A. Empirical Flux Determination Method Description and Applicability

Aerodynamic Method

Study authors employed the aerodynamic method, also referred to as the "flux-gradient" method, as one of the techniques for estimating flux rates from fields treated for this field study given the available data. In the aerodynamic method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from 0.5 to 10 feet. Likewise, temperature and wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. These relationships are then incorporated into an equation to estimate flux.

The minimum fetch requirement that the fetch is 100 times the highest height of the air sampler (*i.e.*, 150 m) for this method to be valid **was not** satisfied at any of the times during the study, therefore the reviewer did not evaluate the flus rates based on this method. The aerodynamic method used to estimate flux and related equations are presented in Majewski et al., 1990.

Integrated Horizontal Flux Method

The integrated horizontal flux method, also referred to as the "mass balance" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the integrated horizontal flux method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from approximately 0.5 to 5 feet. Likewise, wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the air concentration and wind speed following the log law relationships for the atmospheric boundary layer. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the integrated horizontal flux method is the following expression:

Equation 1 $$P = \frac{1}{x}\int_{Z_0}^{Z_p} \bar{c}\bar{u}\,dz$$

where P is the volatile flux in units of $\mu g/m^2 \cdot s$, $\bar{c}$ is the average pesticide residue concentration in units of $\mu g/m^3$ at height Z in units of meters, $\bar{u}$ is the wind speed in units of m/s at height Z, x is the fetch of the air trajectory blowing across the field in units of meters, Z_0 is the aerodynamic surface roughness length in units of meters, Z_p is the height of the plume top in units of meters, and dz is the depth of an incremental layer in units of meters. Following trapezoidal integration, equation 1 is simplified as follows in equation 2 (Yates, 1996):

Equation 2 $$P = \frac{1}{x}\sum_{Z_0}^{Z_P} (A * Ln(z) + B) * (C * Ln(z) + D)dz$$

where A is the slope of the wind speed regression line by ln(z), B is the intercept of the wind speed regression line by ln(z), C is the slope of the concentration regression by ln(z), D is the intercept of the concentration regression by ln(z), z is the height above ground level. Z_p can be determined from the following equation:

Equation 3 $$Z_P = \exp\left[\frac{(0.1 - D)}{C}\right]$$

The minimum fetch requirement of 20 meters for this method to be valid was satisfied at all times. The surface characteristics of the two fields were bare soil and a cotton field with cotton at the 6-inch height. For the most part, the maximum surface roughness length requirement of 0.1 meters was satisfied. However, the surface roughness for the cotton field (0.15 m) was slightly above this requirement.

B. Temporal Flux Profile

The flux determined from the registrant and reviewer for each sampling period after the application is provided in **Table 5**.

Table 5. Field volatilization flux rates of dicamba at the bare ground plot

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer	Registrant (µg/m²·s)	Empirical Flux Determination Method	Notes
Application	10/4/16 12:11 – 12:31	0.33	-	0.023	ID	
1	10/4/16 12:34 – 15:33	2.98	0.001649	0.001665	IHF	
2	10/4/16 15:33 – 19:01	3.47	0.001228	0.001215	IHF	
3	10/4-5/16 19:01 – 7:01	12.00	0.000175	0.000179	IHF	
4	10/5/16 7:01 – 18:31	11.50	0.000231	0.000222	IHF	
5	10/5-6/16 18:32 – 7:01	12.48	0.000096	0.000099	IHF	
6	10/6/16 7:03 – 18:30	11.45	0.000084	0.000095	IHF	AB
7	10/6-7/16 18:32 – 7:00	12.47	0.000003	0.000001	IHF	

Data obtained from Table 8, p. 48; Table 11, p. 51; Table 15, p. 55; and Table 19, p. 59 in the study report and the accompanying Excel spreadsheets.

*Methods legend: ID = Indirect method, IHF = Integrated Horizontal Flux.
Notes
A The dicamba concentration value determine for the sampler at 0.15 m during sampling period 6 was determined to be an outlier and excluded from the calculations (p. 37 and Table 13, p. 53).
B A precipitation event occurred during the 6th sampling period.

Table 6. Field volatilization flux rates of dicamba at the cotton plot

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer	Registrant ($\mu g/m^2 \cdot s$)	Empirical Flux Determination Method	Notes
Application	10/4/16 11:20 – 11:55	0.58	-	0.031	ID	
1	10/4/16 11:59 – 15:32	3.55	0.001920	0.001954	IHF	A
2	10/4/16 15:34 – 19:00	3.43	0.001277	0.001302	IHF	
3	10/4-5/16 19:02 – 7:01	11.98	0.000152	0.000162	IHF	
4	10/5/16 7:02 – 18:30	11.47	0.000128	0.000115	IHF	A
5	10/5-6/16 18:33 – 7:00	12.45	0.000124	0.000123	IHF	
6	10/6/16 7:01 – 18:31	11.50	0.000054	0.000067	IHF	AB
7	10/6-7/16 18:32 – 7:00	12.47	0.000014	0.000000	IHF	A

Data obtained from Table 8, p. 48; Table 11, p. 51; Table 16, p. 56; and Table 20, p. 60 in the study report and the accompanying Excel spreadsheets.
*Methods legend: ID = Indirect method, IHF = Integrated Horizontal Flux.
Notes
A The dicamba concentration values determine for the samplers at 0.55 m (sampling period 1), 0.33 m (period 4), 0.15 m (period 6), and 1.5 m (period 7) were determined to be outliers and excluded from the calculations (p. 37 and Table 13, p. 53).
B A precipitation event occurred during the 6th sampling period.

Maximum flux rates occurred shortly after application during the first sampling period, 0 to 3 hours after application. For the bare ground plot, the maximum flux rates were 0.001665 $\mu g/m^2 \cdot s$ for the Integrated Horizontal Flux Method. For the cotton plot, the maximum flux rates were 0.001954 $\mu g/m^2 \cdot s$ for the Integrated Horizontal Flux Method. A precipitation event during the sixth sampling period (pp. 34 and 37) may have contributed to muting the typically observed diurnal cycle.

As indicated in **Tables 5 and 6**, several outlying data points were not included in the analysis when calculating flux values (p. 37). Deleted Studentized Residual (DSR) values were calculated for the concentration data, and data points with DSR values greater than 6 were flagged for further inspection. Five outliers were ultimately excluded from the calculations.

All R-squared values for concentration and wind speed regressions were 0.92 or greater except for the concentration profiles for Period 7. The R-squared values for concentration in Period 7 were 0.41 and 0.74 for the bare ground plot and cotton plot, respectively. R-squared values for temperature for the bare ground plot were incorrectly reported as the same values reported for concentration (Appendix 8, p. 275). R-squared values for temperature for the cotton plot were 0.89 or greater except for that for period 5, for which the R-squared value was 0.39 (Appendix 8, p. 277).

III. Study Deficiencies and Reviewer's Comments

1. The registrant used a different approach to calculate Z_p, the top of the concentration plume than that recommended by EPA when calculating volatilization flux rates using the Integrated Horizontal Flux method. The registrant used:

$$Z_p = \exp\left(\frac{-D}{C}\right)$$

   C and D are the slope and intercept of the log-linear concentration regression and removed the 0.1 from the equation. The 0.1 represents the concentration at the top of the plume, which is a carryover from the use of this technique for estimating flux rates for fumigants, which typically have much higher concentrations than those anticipated for semi-volatile chemicals like dicamba. The revised equation is acceptable to the reviewer and does not significantly impact the estimate of flux rates.

2. A summary table was provided for the recovery of dicamba from fortified PUF samples (Appendix 6, Table 5, p. 139). The study reports that individual samples from this table can be found in the recovery data tables (Appendix 6, p. 131). While some samples do appear in the data recovery tables (Appendix 6, p. 209), it does not appear that all recovery samples are included in this table.

3. During the cotton study, dicamba concentration values, which were determined to be outliers [the samplers at 0.55 m (sampling period 1), 0.33 m (period 4), 0.15 m (period 6), and 1.5 m (period 7)], were excluded from the study author calculations. The reviewer only removed the samples from periods 4 and 7 when estimating flux rates and the impact did not result in significantly differences between the study author and reviewer flux rates for periods 1 and 6, where the samples were retained.

4. A rain event occurred during sampling period 6 which may have reduced the emissions of dicamba for that timeframe. Given that this occurred during the morning of Day 3, when the flux rates are expected to be lower than the first two days, this does not appear to have significantly impacted the results of the study.

5. Dicamba was detected in pre-application samples collected from both plots at low concentrations. Concentrations used to estimate flux using the indirect method were corrected to account for the background concentrations. Concentrations used to estimate

flux using the integrated horizontal flux method were not corrected, as they were several orders of magnitude higher than the background concentrations.

6. The minimum fetch required for use of the aerodynamic method was not satisfied. As a result, the reviewer did not include the study authors flux estimates using this method.

7. Analytical method validation was performed, but the method was not independently validated. A method validation study should be completed from an independent laboratory separate from and prior to the analysis of the test samples to verify the analytical methods.

8. Soil bulk density and organic matter content were reported at only a single depth of 0-6 inches (Table 1, p. 41).

9. R-squared values for the temperature regression for the bare ground plot are incorrectly reported as being the values for the concentration regression (Appendix 8, p. 275).

IV. References

Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.

Majewski, M.S., Glotfelty, D.E., Kyaw Tha Paw U., Seiber, JN. 1990. A field comparison of several methods for measuring pesticide evaporation rates from soil. Environmental Science and Technology, 24:1490-1497.

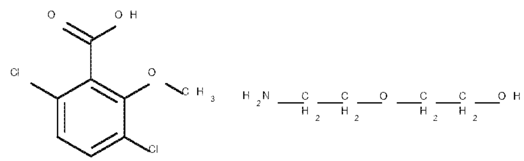
Reiss, R. and Popovic, J. (2017). Deposition and Air Concentration Modeling for Dicamba Formulation MON 76980 Mixed with Formulation MON 79789. Exponent, Inc. Alexandria, Virginia. Sponsored by Monsanto, St. Louis, Missouri. Monsanto Study ID: STC-2016-0545. MRID 50578903.

Wilson, J.D., and Shum. W.K.N. 1992. A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. Agriculture Forest Meteor. Vol 57:281-295.

Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and Yates, M.V. 1996. Methyl Bromide Emissions from a Covered Field: II. Volatilization," Journal of Environmental Quality, 25: 192-202.

Attachment 1: Chemical Names and Structures

Dicamba-diglycolamine and Its Environmental Transformation Products. [A]

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
PARENT						
Dicamba-diglycolamine (Diglycolamine salt of dicamba)	IUPAC: 3,6-Dichloro-o-anisic acid-2-(2-aminoethoxy)ethanol CAS: 2-(2-Aminoethoxy)ethanol;3,6-dichloro-2-methoxy-benzoic acid CAS No.: 104040-79-1 Formula: $C_{12}H_{17}Cl_2NO_5$ MW: 326.17 g/mol SMILES: COc1c(Cl)ccc(Cl)c1C(=O)O.NCCOCCO		Field volatility	50578902	NA	NA
MAJOR (>10%) TRANSFORMATION PRODUCTS						
No major transformation products were identified.						
MINOR (<10%) TRANSFORMATION PRODUCTS						
No minor transformation products were identified.						
REFERENCE COMPOUNDS NOT IDENTIFIED						
All compounds used as reference compounds were identified.						

[A] AR means “applied radioactivity”. MW means “molecular weight”. NA means “not applicable”.

Attachment 2: Statistics Spreadsheets and Graphs

Supporting spreadsheet files for the Integrated Horizontal Flux Method accompany the review.

1. Validation spreadsheet for the bare ground plot following the Integrated Horizontal Flux Method

128931_50578902

2. Validation spreadsheet for the cotton plot following the Integrated Horizontal Flux Method

128931_50578902

Attachment 3: Field Volatility Study Design and Plot Maps

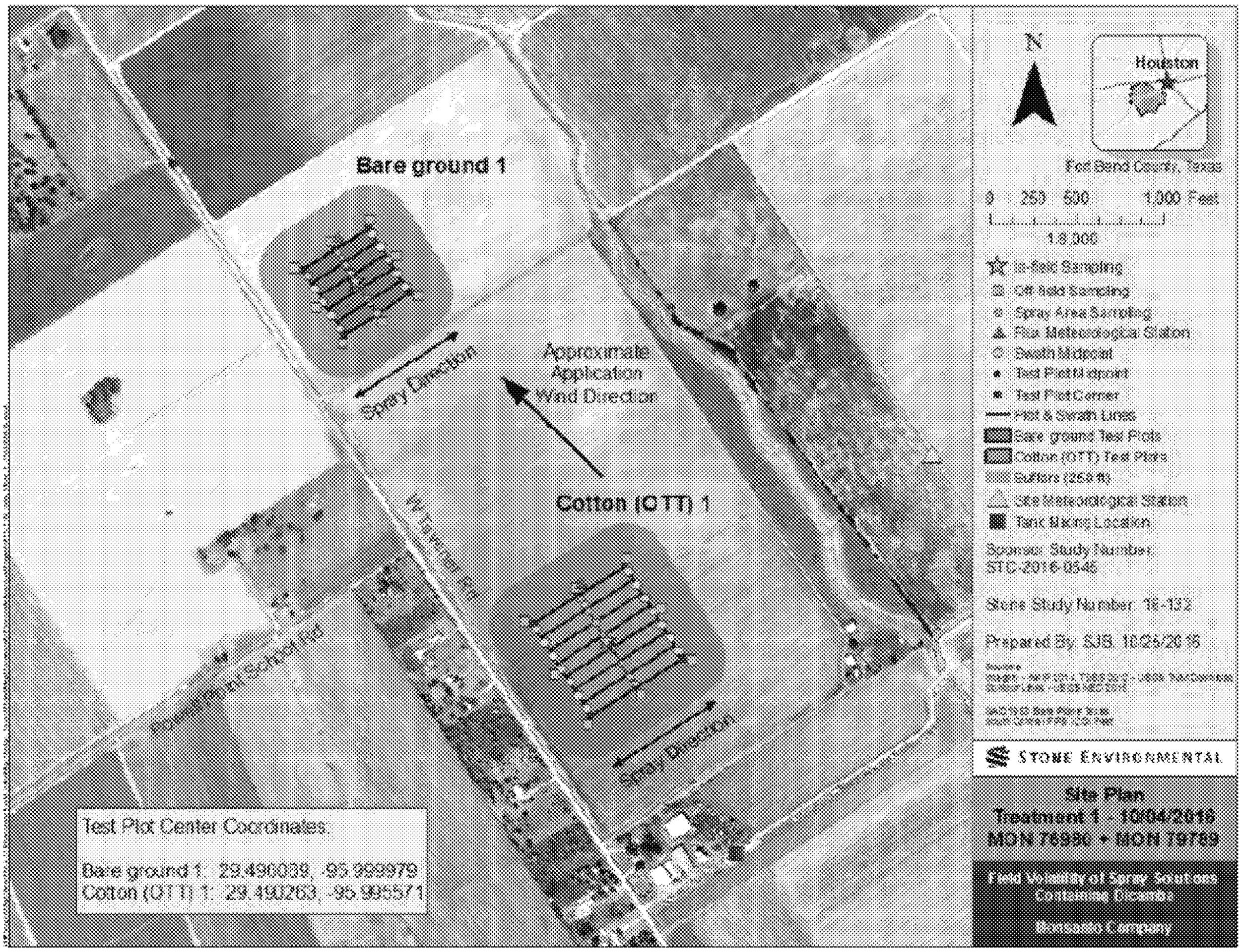


Figure obtained from Figure 3, p. 65, of the study report.

Figure 1. Representative Site Layout – Pre-emergence

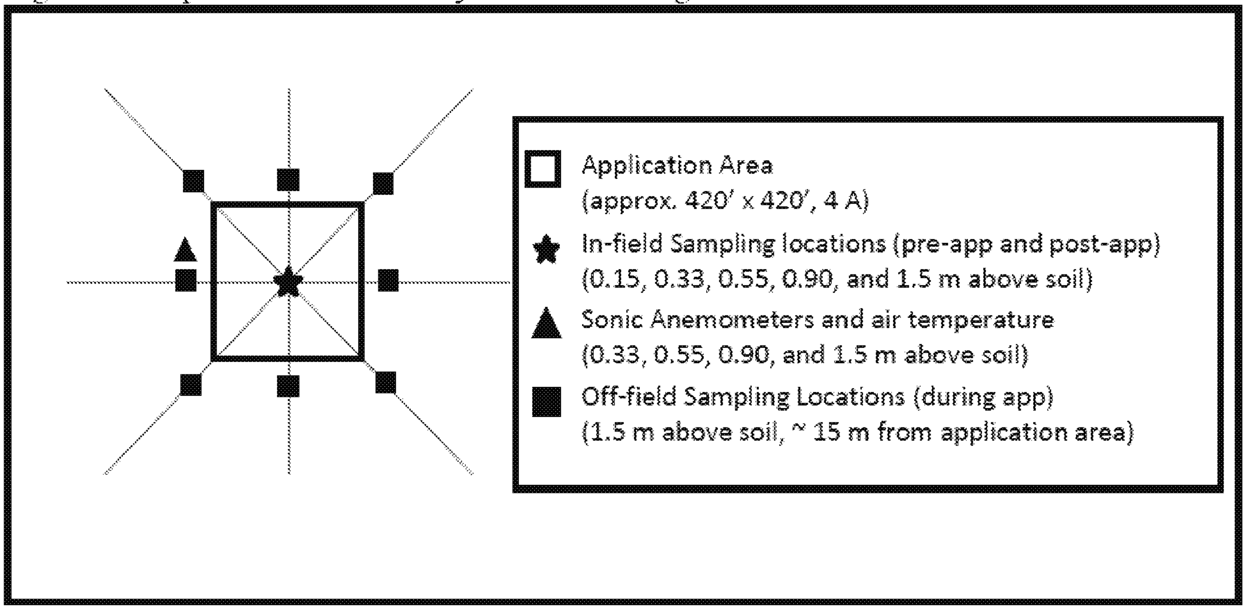
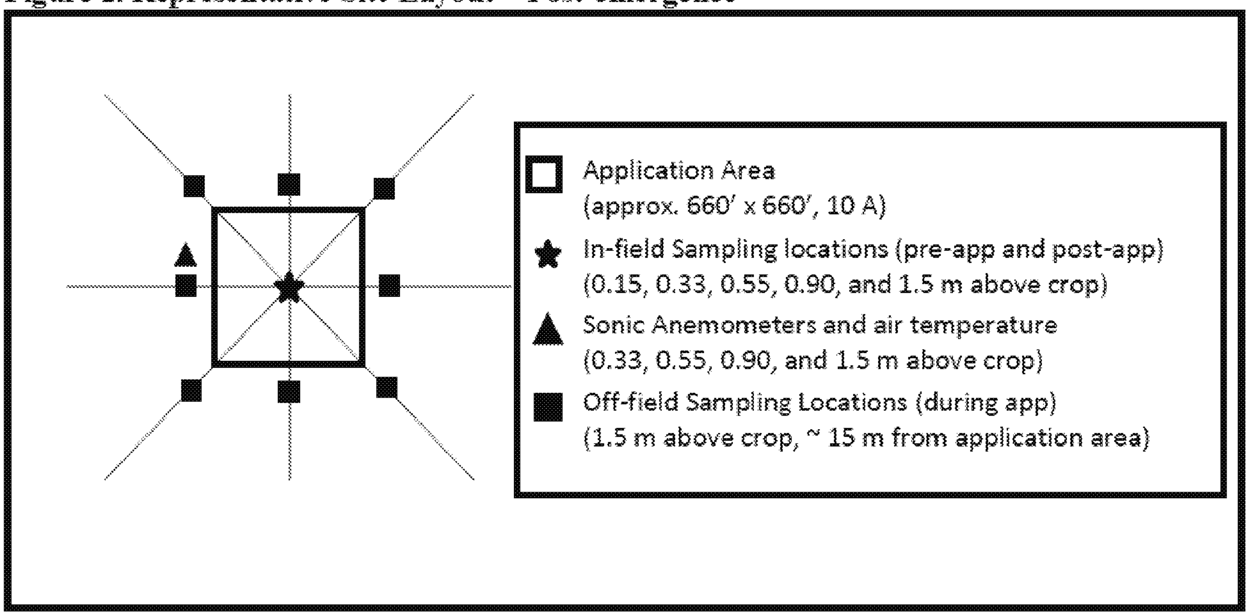


Figure 2. Representative Site Layout – Post-emergence



Figures obtained from Appendix 10, Figures 1 and 2, p. 312 of the study report.

Attachment 4: Calculations and Index of Variables Used in Flux Determination Methods

Aerodynamic Method

Equation x_1 $$Flux = \frac{-(0.42)^2(c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m \phi_p \ln\left(\frac{z_{top}}{z_{bottom}}\right)^2}$$

Flux ($\mu g/m^2s$): volatile flux of pesticide from release source surface

c_{ztop} ($\mu g/m^3$): concentration at the top sampler adjusted according to the regression of concentration vs. ln (height)

$c_{zbottom}$ ($\mu g/m^3$): concentration at the bottom sampler adjusted according to the regression of concentration vs. ln (height)

u_{ztop} (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. ln (height)

$u_{zbottom}$ (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. ln (height)

ϕ_m and ϕ_p (dimensionless): Internal Boundary Layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i:

Equation x_2 $$R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\frac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] + (u_{ztop} - u_{zbottom})^2}$$

where:

T_{ztop}: Temperature at the top sampler adjusted according to the regression of temperature vs. ln (height)

$T_{zbottom}$: Temperature at the bottom sampler adjusted according to the regression of temperature vs. ln (height)

R_i (dimensionless): Richardson Number

if $R_i > 0$ (for Stagnant/Stable IBL)

$$\phi_m = (1 + 16R_i)^{0.33} \text{ and } \phi_p = 0.885(1 + 34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)

$$\phi_m = (1 - 16R_i)^{-0.33} \text{ and } \phi_p = 0.885(1 - 22R_i)^{-0.4}$$

Integrated Horizontal Flux Method

Equation x_3 $$P = \frac{1}{x}\sum_{Z_0}^{Z_P}(A * Ln(z) + B) * (C * Ln(z) + D)dz$$

P ($\mu g/m^2 s$): volatile flux of pesticide from release source surface
z (m): height above ground level
A (s^{-1}): slope of the wind speed regression line by ln(z)
B (m/s): intercept of the wind speed regression line by ln(z)
C ($\mu g/m^4$): slope of the concentration regression by ln(z)
D ($\mu g/m^3$): intercept of the concentration regression by ln(z)
Z_0 (m): aerodynamic surface roughness length of release source surface
Z_p (m): volatile plume top height; calculated from the following equation:

Equation x_4

$$Z_P = \exp\left[\frac{(0.1 - D)}{C}\right]$$